

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2005-126534

(43)Date of publication of application : 19.05.2005

(51)Int.Cl.

C08L 75/04
B29C 41/18
// (C08L 75/04
C08L 35:00)
B29K 75:00
B29L 31:58

(21)Application number : 2003-362460

(71)Applicant : SANYO CHEM IND LTD
TOYOTA MOTOR CORP

(22)Date of filing : 22.10.2003

(72)Inventor : OMORI HIDEKI
NISHIOKA SHOGO
FUKAMACHI TAKESHI
MARUYAMA DAICHI
NOMURA MASATO

(54) RESIN POWDER COMPOSITION FOR SLUSH MOLDING AND MOLDING

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain thermoplastic polyurethane resin powder for slush molding by finding an antiblocking agent not to cause mold deposit and using the antiblocking agent by considering that an antiblocking agent has a problem of causing mold deposit, increasing mold release resistance with it, reducing gloss on the surface of obtained skin and deteriorating an appearance in slush molding.

SOLUTION: The resin powder composition for slush molding comprises thermoplastic polyurethane resin powder as a main component and contains powder of fine particles of a maleimide copolymer not melting at a molding temperature and having crosslinked structure. For example, a copolymer of N-cyclohexylmaleimide and 2-hydroxyethyl (meth)acrylate, which is crosslinked with hexamethylene diisocyanate and/or isophorone diisocyanate is used as the fine particle powder.

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]

A resin powder constituent for slush molding containing maleimide copolymer (A0) particle powder (A) which makes thermoplastic polyurethane resin powder (B) a subject, and does not fuse with molding temperature, but has the structure of cross linkage.

[Claim 2]

The resin powder constituent according to claim 1 whose mean particle diameter of the above-mentioned particle powder (A) is 0.1 micrometers or more 100 micrometers or less.

[Claim 3]

The resin powder constituent according to claim 1 or 2 in which it comes to construct a bridge over said maleimide copolymer (A0) by polyisocyanate.

[Claim 4]

Said maleimide copolymer (A0), It comes to construct a bridge over copolymer of N-cyclohexylmaleimide and 2-hydroxyethyl (meta) acrylate by hexamethylene di-isocyanate and/or isophorone diisocyanate, and is a resin powder constituent of any of a certain Claims 1-3, or a description.

[Claim 5]

one of Claims 1-4 to which it comes to carry out the dry blend of said thermoplastic polyurethane resin powder (B) and said maleimide copolymer-particles powder (A) with an addition auxiliary agent (D) added if needed -- a resin powder constituent of a description.

[Claim 6]

one of Claims 1-5 which said maleimide copolymer-particles powder (A) comes to contain 5 or less % of the weight 0.1% of the weight or more to said thermoplastic polyurethane resin powder (B) -- a resin powder constituent of a description.

[Claim 7]

A resin powder constituent of any of a certain Claims 1-6 or a description of a number average molecular weight of said maleimide copolymer-particles powder (A) or less [5,000 or more] by 20,000.

[Claim 8]

Urethane resin mold goods which consist of a resin powder constituent for slush molding of any of Claims 1-7, or a description.

[Translation done.]

* NOTICES *

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the resin powder constituent for slush molding which is suitable as a raw material for shaping of automobile interior parts, such as an instrument panel and a door trim, and which makes thermoplastic polyurethane resin powder a subject.

[Background of the Invention]

[0002]

Conventionally, a VCM/PVC system powder slush molding article is used as a skin material of automobile interior parts, such as an instrument panel and a door trim, in many cases.

[0003]

However, if long term use of the VCM/PVC system material is carried out, the plasticizer contained in inside by heat, light, etc. will shift to the surface, and a soft feeling will be spoiled. The problem that an incinerator corrodes is pointed out by the hydrogen chloride gas emitted when carrying out incineration—after motor vehicle cassation processing.

In order to solve these problems, development of the powder slush molding material which makes thermoplastic polyurethane resin powder a subject is furthered. A powder slush molding method is the method of fabricating a skin material by filling up with and rotating powder in the metallic mold heated at 200–240 **, making a metallic mold inner surface weld powder, making it discharge from a metallic mold the end of non-welding powder, and collecting.

[0004]

However, if the thermoplastic polyurethane resin powder for slush molding is neglected, blocking will be caused temporally and particulate flow kinesis will worsen. In order to improve these phenomena, the trial of adding maleimide polymer-particulates powder or adding the thermoplastic resin powder which does not carry out thermofusion below 160 ** as an antiblocking agent, is made (for example, refer to the patent documents 1 and patent documents 2.).

[0005]

[Patent documents 1] JP,H10-77403,A (Claims, the 3–4th page)

[Patent documents 2] JP,2000-17033,A (Claims, the 5–6th page)

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0006]

However, the thermoplastic polyurethane resin powder using the above-mentioned antiblocking agent raises metallic mold dirt, and the gloss of the outside skin obtained by mold release resistance becoming heavy in connection with it falls, and it has the problem that appearance gets worse.

SUBJECT of this invention finds out the antiblocking agent which does not raise metallic mold dirt, and there is in providing the thermoplastic polyurethane resin powder for slush molding using this.

[Means for Solving the Problem]

[0007]

As a result of inquiring wholeheartedly, when adding maleimide copolymer powder which has the structure of cross linkage in a thermoplastic polyurethane resin powder constituent, this invention person finds out that metallic mold dirt is not raised but blocking can also be prevented, and came to complete this invention.

[0008]

That is, this invention is a resin powder constituent for slush molding containing maleimide copolymer (A0) particle powder (A) which makes thermoplastic polyurethane resin powder (B) a subject, and does not fuse with molding temperature, but has the structure of cross linkage.

[Effect of the Invention]

[0009]

If the resin powder constituent of this invention which contains the maleimide copolymer-particles powder which has the structure of cross linkage is used for slush molding, Without spoiling the melting nature of the constituent at the time of shaping, metallic mold dirt can be prevented and the effect that aggravation of the moldability at the time of fabricating continuously and the debasement of shaping epidermis are avoidable is done so. Since the above-mentioned effect is done so, the resin powder constituent of this invention is useful as a charge of slush molding material.

This invention is explained below.

[Best Mode of Carrying Out the Invention]

[0010]

the maleimide copolymer (A0) (the following -- only (A0) -- **** -- it says) which has the structure of cross linkage used by this invention, as an indispensable constituent -- a maleimide monomer (a01) (the following -- only (a01) -- **** -- it says). it consisting of a maleimide monomer, a monomer (a02) (the following -- only (a02) -- **** -- it says) which has polymerizable active hydrogen, and a cross linking agent component (a03) (the following -- only (a03) -- **** -- it says), and, the monomer (a04) (the following -- only (a04) -- **** -- it says) which is as copolymerizable as a maleimide monomer and does not have active hydrogen as occasion demands can be made into a constituent.

[0011]

As an example of the above-mentioned maleimide monomer (a01), N-aliphatic hydrocarbon group maleimide [N-methylmaleimide, N-ethylmaleimide, N-isopropylmaleimide, N-n-butylmaleimide, N-isobutylmaleimide, N-t-butylmaleimide, N-decylmaleimide, N-dodecylmaleimide,] and N-alicyclic hydrocarbon group maleimide [, such as N-octadecylmaleimide,] [N-cyclohexylmaleimide,], such as N-2-ethylhexyl maleimide and N-cyclododecylmaleimide, N-aromatic hydrocarbon group maleimide [N-phenylmaleimide, N-o-methylphenyl maleimide, N-benzylmaleimide, N-phenyl-2-chloromaleimide, N-benzyl-2-methylmaleimide], etc. are mentioned. In these, from a viewpoint of compatibility with urethane resin, N-alicyclic hydrocarbon group maleimide and N-aliphatic hydrocarbon group maleimide are preferred, and N-cyclohexylmaleimide is still more preferred.

[0012]

The following are mentioned as the above-mentioned maleimide monomer and a monomer (a02) which has copolymerizable active hydrogen.

(a021) Hydroxyl content vinyl monomer

(1) (meta) Acrylate ester

2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, Ethylene glycol mono- (meta) acrylate, propylene glycol mono- (meta) acrylate, neopentyl glycol mono- (meta) acrylate, TORIMECHI roll pro pansy (meta) acrylate, polyethylene-glycol mono- (meta) acrylate, etc.

(2) Alcohols

(Meta) Allyl alcohol, clo chill alcohol, isoclo chill alcohol, a 1-buten-3-ol, a 2-butene-1-ol, 2-butene-1, 4-diol, propargyl alcohol, 2-hydroxyethyl propenyl ether, **** allyl ether, etc.

(3) Nitrogen-containing monomer

N-methylol(metha)acrylamide etc.

(4) In addition to this

Hydroxystyrene etc.

(a022) Amino group content vinyl monomer

Aminoethyl (meta) acrylate, acrylamide (meta), etc.

(a023) Carboxyl group containing vinyl monomer

(Meta) Acrylic acid, maleic acid (anhydrous), maleic acid monoalkyl ester, Carboxyl group containing vinyl monomers, such as fumaric acid, fumaric acid monoalkyl ester, crotonic acid, itaconic acid, itaconic acid monoalkyl ester, itaconic acid glycol monoether, citraconic acid, citraconic acid monoalkyl ester, and cinnamic acid etc.

A hydroxyl (a021) content vinyl monomer is preferred in the above, hydroxyl content (meta) acrylate ester is still

more preferred, and 2-hydroxyethyl (meta) acrylate is the most preferred.

[0013]

As the above-mentioned cross linking agent component (a03), organic polyisocyanate (a031), a poly epoxy compound (a032), and a polycarboxylic acid compound (a033) are mentioned. A thing desirable in these is organic polyisocyanate (a031).

as the above-mentioned organic polyisocyanate (a031) (the following — only (a031) — **** — it says), what is used for polyurethane manufacture from the former can be used. In (a031), have 2-5 pieces or an isocyanate group (NCO group) beyond it (preferably two pieces). The aliphatic series polyisocyanate of the carbon numbers (carbon in an NCO group is excluded it is the same as that of the following) 2-18, The alicyclic polyisocyanate of the carbon numbers 4-15, the aroma aliphatic series polyisocyanate of the carbon numbers 8-15, and the aromatic polyisocyanate of the carbon numbers 6-20. The denaturation objects (a carbodiimide denaturation object, a urethane denaturation object, an urethodione denaturation object, an isocyanurate denaturation object, etc.) of such polyisocyanates and two or more sorts of these mixtures are contained.

[0014]

As aliphatic series polyisocyanate, diisocyanate, for example, ethylene di-isocyanate, Tetramethylene di-isocyanate, hexamethylene di-isocyanate (HDI), Dodeca methylene di-isocyanate, 2,2,4-trimethylhexane diisocyanate, Lysine diisocyanate, 2,6-diisocyanatomethyl caproate, Bis(2-isocyanatoethyl)fumarate, bis(2-isocyanatoethyl)carbonate, and 2-isocyanatoethyl-2,6-diisocyanato hexanoate; tri-isocyanate, for example, 1, 6-11-undecane triisocyanate, etc. are mentioned.

[0015]

As alicyclic polyisocyanate, isophorone diisocyanate (IPDI), The dicyclohexyl methane- 4, 4'-diisocyanate (hydrogenation MDI), Cyclohexylene diisocyanate, methyl cyclohexylene diisocyanate, bis(2-isocyanatoethyl)-4-cyclohexylene- 1, 2-dicarboxylate and 2, and 5- or 2, and 6-norbornane diisocyanate etc. are mentioned. aroma — aliphatic series — polyisocyanate — ***** — m — and/or — p — xylene diisocyanate — diethylbenzene — diisocyanate — and — alpha — alpha — ' — alpha — ' — tetramethyl one — xylene diisocyanate — etc. — mentioning — having .

[0016]

As aromatic polyisocyanate, diisocyanate, for example, 1, and 3- and/or 1, 4-phenylene diisocyanate, 2 and 4- and/or 2, 6-tolylene diisocyanate (TDI), -, and/or 4 and 4 '2, 4'-diphenylmethane diisocyanate (MDI), 4,4'-diisocyanatobiphenyl, 3,3'-dimethyl- 4,4'-diisocyanatobiphenyl, 3,3'-dimethyl- 4,4'-diisocyanatodiphenylmethane and 1,5-naphthylene diisocyanate; and the polyisocyanates of three or more organic functions (tri-isocyanate etc.), for example, polyphenyl methane polyisocyanate, (crewed MDI) are mentioned.

[0017]

Organic diisocyanate is [among these] preferred. Non-aromatic (aliphatic series, alicyclic, and aroma aliphatic series) polyisocyanate especially aliphatic series diisocyanate, cycloaliphatic diisocyanate, and these concomitant use are preferred from a light-fast viewpoint. Hexamethylene di-isocyanate, the hydrogenation MDI, and isophorone diisocyanate are the most preferred.

[0018]

As the above-mentioned poly epoxy compound (a032), they may be aliphatic series, alicycle fellows, and heterocyclic or aromatic any.

[0019]

As aromatic polyepoxide (a0321), For example, the glycidyl ether object of polyhydric phenol is mentioned. For example, bisphenol F diglycidyl ether, bisphenol A diglycidyl ether, Bisphenol B diglycidyl ether, bisphenol A D diglycidyl ether, Bisphenol S diglycidyl ether, halogenated-bisphenol-A diglycidyl, Tetrachloro bisphenol A diglycidyl ether, catechin diglycidyl ether, Resorcinol diglycidyl ether, hydroquinone diglycidyl ether, Pyrogallol triglycidyl ether, 1,5-dihydroxynaphthalene diglycidyl ether, Dihydroxybiphenyl diglycidyl ether, the octachloro- 4, 4'-dihydroxybiphenyl diglycidyl ether, Phenol or the glycidyl ether object of cresol novolak resin. The poly glycidyl ether object of the polyphenol obtained by the condensation reaction of 2 mol of bisphenol A, the diglycidyl ether object and phenol which are obtained from the reaction of 3 mol of epichlorohydrin, glyoxal, a glutaraldehyde, or formaldehyde, And the poly glycidyl ether object of the polyphenol obtained by the condensation reaction of resorcinol and acetone is mentioned.

In this invention, as said aromatic polyepoxide. For example, the diglycidyl urethane compound obtained by the addition reaction of tolylene diisocyanate or diphenylmethane diisocyanate, and glycidol, The diglycidyl ether object

of the alkylene oxide (ethylene oxide or propylene oxide) addition of glycidyl group content polyurethane (pre) polymer and bisphenol A acquired by making polyol react to said two reactants is also included.

[0020]

As heterocyclic polyepoxide (a0322), tris glycidyl melamine is mentioned, for example.

[0021]

As alicycle fellows' polyepoxide (a0323), For example, vinylcyclohexene dioxide, limonenedioxide, dicyclopentadienedioxide, Bis(2,3-epoxy cyclopentyl)ether, an ethylene glycol BISUEPOKISHIJI cyclopentyl yell, 3,4-epoxy-6-methylcyclohexylmethyl-3',4'-epoxy-6'-methylcyclohexane carboxylate, A bis(3,4-epoxy-6-methylcyclohexylmethyl)horse mackerel peat and a bis(3,4-epoxy-6-methylcyclohexylmethyl)butylamine are mentioned. As alicycle fellows' polyepoxide, the core hydrogenation ghost of said aromatic polyepoxide compound is also included.

[0022]

As polyepoxide (a0324) of aliphatic series, the poly glycidyl ether object of polyhydric aliphatic alcohol, the poly glycidyl ester body of multivalent fatty acid, and glycidyl fatty amine are mentioned, for example.

As a poly glycidyl ether object of polyhydric aliphatic alcohol, For example, ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, Tetramethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, Polypropylene glycol diglycidyl ether, trimethylolpropane triglycidyl ether, pentaerythritol tetraglycidyl ether, and sorbitol polyglycidyl ether are mentioned.

As a poly glycidyl ester body of multivalent fatty acid, a diglycidyl horse mackerel peat is mentioned, for example.

As glycidyl fatty amine, N,N,N',N'-tetraglycidyl ether hexamethylenediamine is mentioned, for example.

In this invention, the polymer (**) of glycidyl (meta) acrylate is also included as aliphatic series.

[0023]

Aliphatic series and alicycle fellows polyepoxide are [among these] preferred.

[0024]

As a polycarboxylic acid compound (a033), What is conventionally used for polyester resin composition can be used. For example, aliphatic-dicarboxylic-acid [succinic acid of the carbon numbers 4-15, adipic acid,], such as sebacic acid, glutaric acid, azelaic acid, maleic acid, and fumaric acid, The aromatic dicarboxylic acid of the carbon numbers 8-12 [terephthalic acid, isophthalic acid], etc., Tricarboxylic acid [trimellitic acid] The ester plasticity derivative [acid anhydride of these, lower alkyl ester (dimethyl ester, diethyl ester, etc.), and two or more sorts of these mixtures are mentioned.

[0025]

Aliphatic dicarboxylic acid is [among these] preferred.

[0026]

As a monomer (a04) which is as copolymerizable as the above-mentioned maleimide monomer, and does not have active hydrogen, The monomer of styrene systems, such as styrene and alpha-methylstyrene, methyl acrylate (meta), (Meta) The alkyl ester of acrylic ester (meta), such as butyl acrylate and 2-ethylhexyl acrylate (meta), acrylic (meta) nitril, vinyl acetate, a maleic anhydride, maleic acid, and fumaric acid is mentioned.

[0027]

the weight ratio of the above (a01), (a02), (a03), and (a04) -- from a viewpoint of compatibility with urethane resin -- desirable -- 59 to 98:1 to 20:0.1 to 1:0-20 -- it is 74.4 to 94.7:5 to 15:0.2 to 0.6:0.1-10 still more preferably.

(a02) the equivalent ratio of the functional group reacted to this active hydrogen to inner active hydrogen (a03) -- from a viewpoint of mold staining property -- desirable -- 1.0:0.01 to 0.5 -- it is 1.0:0.03-0.2 still more preferably.

[0028]

As a desirable example of a maleimide copolymer (A0) of having the structure of cross linkage, What constructed the bridge by alicycle fellows diisocyanate in the copolymer of N-cyclohexylmaleimide, what constructed the bridge by aliphatic series diisocyanate in the copolymer of 2-hydroxyethyl (meta) acrylate and N-ethyl malei mide, and 2-hydroxyethyl (meta) acrylate is mentioned. These maleimide copolymer (A0) may use one sort alone, and may mix and use two or more sorts. Especially a desirable thing constructs a bridge by hexamethylene di-isocyanate and/or isophorone diisocyanate in the copolymer of N-cyclohexylmaleimide and 2-hydroxyethyl (meta) acrylate from compatibility with polyurethane resin.

[0029]

As a manufacturing method of the maleimide copolymer (A0) which has the structure of cross linkage, the following two kinds of methods are mentioned, for example.

(1) Make the active hydrogen portion and cross linking agent component (a03) of a maleimide monomer and the monomer (a02) which has copolymerizable active hydrogen react first. How to add this resultant, a maleimide monomer (a01), and the monomer (a04) that is as copolymerizable as a maleimide monomer and does not have active hydrogen as occasion demands, and for the appropriate back to polymerize it, and to obtain (A0). Add (a04) by (2), (a01) and (a02), and necessity, it is made to polymerize, and a polymer is obtained. this polymer — (a03) — in addition, crosslinking reaction is performed — making (A0) — the method of obtaining.

(1) is preferred among the above.

[0030]

(a02) The active hydrogen in the polymer which consists of (a04) by the reaction temperature of inner active hydrogen and a cross linking agent component (a03), (a01) and (a02), and necessity, and 50–130 °C of reaction temperature of (a03) are 80–110 °C preferably.

A solvent and a catalyst can be used if needed. As an example of this solvent, ketones [MEK, MIBK], etc. and ester solvent [methyl acetate,], such as ethyl acetate and butyl acetate, an aromatic solvent [toluene, xylene], etc., a nitrile system solvent [acetonitrile] etc., an ethers solvent [a tetrahydrofuran, petroleum ether, diethylether], etc., and other solvents [DMF] etc. are mentioned.

As an example of this catalyst, an organic metallic compound [diethyltin dilaurate, neo decanoic acid bismuth], etc. and amines [triethylamine, triethyltriamine], etc. are mentioned.

30 °C — 120 °C of reaction temperature of the reaction used (a01), (a02), and if needed (a04) is 40–90 °C preferably. A solvent and a polymerization initiator, and a chain transfer agent can be used if needed. The above-mentioned solvent can be used as this solvent. This polymerization initiator can use a publicly known initiator, for example, an azo compound and a peroxide are mentioned. Publicly known things, such as lauryl mercaptan, can be used as a chain transfer agent.

[0031]

As a manufacturing method of the particle powder (A) which consists of a maleimide copolymer (A0) which has the structure of cross linkage, the following methods are mentioned, for example.

(1) Obtain the impalpable powder of a maleimide monomer (a01) by suspension polymerization etc. first.

After an appropriate time, The resultant which consists of the active hydrogen portion and cross linking agent component (a03) of a maleimide monomer and the monomer (a02) which has copolymerizable active hydrogen by the impalpable powder (a01) necessity for a maleimide monomer. How to obtain the particle powder (A) which consists of adding the monomer (a04) which is as copolymerizable as a maleimide monomer and does not have active hydrogen, and polymerizing it (A0).

(2) And it was obtained by suspension polymerization etc. (a01), add (a04) by (a02) and necessity, make it polymerize, and obtain the polymer of particle powder. How to add (a03) to this polymer, to make crosslinking reaction perform, and to obtain particle powder (A).

(3) How to obtain particle powder (A) by grinding after obtaining (A0) by mass polymerization.

(1) is preferred among the above.

[0032]

These maleimide copolymer-particles powder (A) may use one sort alone, and may mix and use two or more sorts.

As a blending ratio of the above-mentioned particle powder (A), from the mobility (powder flow nature) of a resin powder constituent, and a viewpoint of blocking. It is 0.6 % of the weight or more still more preferably 0.1% of the weight or more preferably to thermoplastic polyurethane resin powder (B), and is 1.5 or less % of the weight still more preferably 5 or less % of the weight preferably from a viewpoint of metallic mold dirt.

[0033]

As particle diameter of the above-mentioned particle powder (A), from a fluid (powder flow nature) viewpoint of a resin powder constituent, it is 0.5 micrometers or more still more preferably, and 0.1 micrometers or more of 100 micrometers or less are 50 micrometers or less still more preferably preferably.

Although the shape in particular of the above-mentioned particle powder (A) is not asked, it is desirable that it is close to a globular form or it from the field of the flow nature of the material at the time of shaping.

[0034]

As a number average molecular weight of the above-mentioned maleimide copolymer (A0), from a heat-resistant viewpoint, it is 7,000 or more still more preferably, and is 18,000 or less still more preferably 20,000 or less preferably from a viewpoint of the thermal fusibility of a resin powder constituent 5,000 or more.

A number average molecular weight here is computable using gel permeation chromatography (GPC) based on the

analytical curve acquired from molecular weight correlation samples, such as polystyrene. A number average molecular weight is measured by this method below.

[0035]

A die temperature is preferred and slush molding of 200–300 °C of the resin powder constituents for slush molding of this invention is carried out at 210–280 °C still more preferably. Maleimide copolymer-particles powder (A) is not fused in this temperature requirement.

The thermoplastic polyurethane resin powder (B) used for this invention can be fused in the above-mentioned temperature requirement.

[0036]

As a manufacturing method of thermoplastic polyurethane resin powder (B) and (only saying (B) below), the following methods are mentioned, for example.

(1) What is manufactured by the method which has the presentation of a urethane bond and urea combination, and to which an isocyanate group end urethane prepolymer and the blocked chain extension agent (for example, ketimine compound) are made to react under water and dispersion stabilizer existence. What was specifically indicated to JP,H8-120041,A etc. can be used.

(2) What is manufactured by the method to which a chain extension agent (for example, diamine and/or glycol) is made to react under the organic solvent in which this urethane prepolymer does not dissolve a urethane prepolymer with the presentation of a urethane bond and urea combination, and dispersion stabilizer existence. What was specifically indicated to JP,H4-202331,A etc. can be used.

(3) Obtain the mass material of thermoplastic polyurethane by making a chain extension agent (low molecule glycol, low molecule diamine) react diisocyanate, the Polymer Division glycol, and if needed. Subsequently, the thing manufactured by the method of carrying out disintegration (for example, the method of cutting through freezing pulverization and the bottom fine pores of a molten state).

The mean particle diameter of (B) is 10–500 micrometers in the range of 70–300 micrometers still more preferably.

50–90 weight-section combination of the (B) is preferably carried out still more preferably 40 to 99 weight section to the weight of the resin powder constituent for slush molding.

[0037]

An addition auxiliary agent (D) is added by the resin powder constituent for slush molding of this invention if needed in the range which does not raise the metallic mold dirt which is an effect peculiar to this invention, but can perform prevention from blocking in addition to the above-mentioned ingredient. As an addition auxiliary agent (D), the paints of publicly known common use, an inorganic bulking agent, a plasticizer, a release agent, an organic bulking agent, a dispersing agent, an ultraviolet ray absorbent (light stabilizer), an antioxidant, etc. can be added. 10–50 weight-section addition of the addition auxiliary agent (D) is preferably carried out still more preferably zero to 60 weight section to the weight of the resin powder constituent for slush molding.

[0038]

As a method of mixing the resin powder constituent for slush molding of this invention, the following methods are mentioned, for example.

(1) How to carry out the dry blend of thermoplastic polyurethane resin powder (B), maleimide copolymer-particles powder (A), and the addition auxiliary agent (D) added if needed.

(2) How to manufacture thermoplastic polyurethane resin powder (B) under the additive agent (D) existence added if needed, and carry out the dry blend of the maleimide copolymer-particles powder (A) after that.

Among these, the method of (1) is preferred.

[0039]

A publicly known powder-mixing device can be used as a mixed device used for the above-mentioned mixing, and both a container rotary type mixer a stationary mixer and a fluid motion type mixer can be used. For example, the method of carrying out a dry blend using a high speed flow type mixer, a double compound paddle type mixer, or a cone type screw mixer as a stationary mixer is known well. In these methods, it is preferred to use a double compound paddle type mixer and a cone type screw mixer.

[0040]

In order to fabricate the resin powder constituent for slush molding of this invention by a slush molding method, For example, oscillating rotation of both the box containing the powder composition of this invention and the metallic mold heated at 200–280 °C can be carried out, and it can be made to be able to solidify after post-cooling

which carried out a melting flow of the powder within the mold, and can carry out suitably by the method of manufacturing epidermis.

As for the skin depth fabricated at the charge of shaping material of this invention, 0.5–1.5 mm is preferred. This epidermis is used suitably for epidermis, such as an automotive interior material, for example, an instrument panel, and a door trim.

[0041]

Hereafter, although the example of manufacture and working example explain this invention still in detail, this invention is not limited to this.

Among an example, especially, as long as there is no notice, all parts shall express a weight section.

[0042]

The example 1 of manufacture

0.5% of the weight of polyvinyl alcohol (88% of saponification degree) solution [300 copies of] was taught to 4 mouth flask provided with the thermometer, the agitator, and the Dimroth condenser. Subsequently, it taught, making 20 copies of methyl ethyl ketone distribute 90 copies of N-cyclohexylmaleimide monomer particles, and ten copies of 2-hydroxyethyl methacrylate. Next, while nitrogen gas replaces the inside of a reactor, after making it polymerize at 65 °C under stirring for 4 hours, the polymer cooled and generated to the room temperature was taken out, it supplied in methanol, and polymer was deposited. Vacuum drying of this was filtered and carried out, and the white granular material (A-1-0) was obtained. Taught these 50 copies of granular materials to the planetary mixer, subsequently taught 0.3 copy of hexamethylene di-isocyanate, it was made to react at 80 °C for 5 hours, and particle powder (A-1) was obtained. The mean particle diameter of particle powder (A-1) was 4 micrometers, and the number average molecular weight was 8,000.

[0043]

The example 2 of manufacture

Taught 50 copies of granular materials (A-1-0) produced by making it be the same as that of the example 1 of manufacture to the planetary mixer, subsequently taught 0.15 copy of isophorone diisocyanate, and 0.15 copy of hexamethylene di-isocyanate, it was made to react at 80 °C for 5 hours, and particle powder (A-2) was obtained. The mean particle diameter of particle powder (A-2) was 3 micrometers, and the number average molecular weight was 12,000.

[0044]

The example 3 of manufacture

Taught 15 copies of 2-hydroxyethyl acrylate, 0.3 copy of hexamethylene di-isocyanate, and 20 copies of methyl ethyl ketone to 4 mouth flask provided with the thermometer, the agitator, and the Dimroth condenser, it was made to react at 80 °C for 5 hours, and the reactant (A-3-0) was obtained.

0.5% of the weight of polyvinyl alcohol (88% of saponification degree) solution [300 copies of] was taught to 4 mouth flask provided with another thermometer, the agitator, and the Dimroth condenser. Subsequently, 85 copies of N-cyclohexylmaleimide monomer particles and 35.3 copies of reactants (A-3-0) were taught. Next, while nitrogen gas replaces the inside of a reactor, after making it polymerize at 65 °C under stirring for 4 hours, the polymer cooled and generated to the room temperature was taken out, it supplied in methanol, and polymer was deposited. Vacuum drying of this was filtered and carried out, and particle powder (A-3) was obtained. The mean particle diameter of particle powder (A-3) was 5 micrometers, and the number average molecular weight was 10,000.

[0045]

The example 4 of manufacture

0.5% of the weight of polyvinyl alcohol (88% of saponification degree) solution [300 copies of] was taught to 4 mouth flask provided with the thermometer, the agitator, and the Dimroth condenser. Subsequently, it taught, making 20 copies of methyl ethyl ketone distribute 85 copies of N-cyclohexylmaleimide monomer particles, and 15 copies of 2-hydroxyethyl acrylate. Next, while nitrogen gas replaces the inside of a reactor, after making it polymerize at 65 °C under stirring for 4 hours, the polymer cooled and generated to the room temperature was taken out, it supplied in methanol, and polymer was deposited. Vacuum drying of this was filtered and carried out, and particle powder (A-4) was obtained. The mean particle diameter of particle powder (A-4) was 5 micrometers, and the number average molecular weight was 7,000.

[0046]

Working example 1

In the Nauta mixer of 100L, coloring thermoplastic-urethane-resin-powder [Sanyo Chemical Industries [Ltd.], Ltd. make] (B-1) 100 copy with a diameter of a centriole of 140 micrometers, Polyethylene GURIKORUJI benzoic ester [Sanyo Chemical Industries [Ltd.], Ltd. make; SANFIKKUSUEB300]. Supplied 20 copies and mixed at 70 ** for 3 hours. subsequently, denaturation dimethylpolysiloxane [—; by Shin-Etsu Chemical Co., Ltd. — after supplying the X22-3710] 0.1 copy and mixing for 1 hour, it cooled to the room temperature. One copy of particle powder (A-1) obtained in the example 1 of after-cooling manufacture was thrown in, and the resin powder constituent for slush molding (S1) was obtained.

[0047]

Working example 2

Except using particle powder (A-2) instead of the particle powder (A-1) of working example 1, it is the same method as working example 1, and the resin powder constituent for slush molding (S2) was obtained.

[0048]

Working example 3

Except using particle powder (A-3) instead of the particle powder (A-1) of working example 1, it is the same method as working example 1, and the resin powder constituent for slush molding (S3) was obtained.

[0049]

Comparative example 1

Except using particle powder (A-4') instead of the particle powder (A-1) of working example 1, it is the same method as working example 1, and the resin powder constituent for slush molding (S4') was obtained.

[0050]

Comparative example 2

Except the particle powder (A-1) of working example 1 using N-cyclohexylmaleimide polymer particle [Nippon Oil & Fats [Co., Ltd.] Co., Ltd. make; NOFUREKKUSU MP-200] instead, it is the same method as working example 1, and the resin powder constituent for slush molding (S5') was obtained.

[0051]

Comparative example 3

Except using styrene resin powder [particle powder the mean particle diameter of 1 micrometer, and given in melting point [of 200 **]; JP,2000-17033,A] instead of the particle powder (A-1) of working example 1, it is the same method as working example 1, and the resin powder constituent for slush molding (S6') was obtained.

[0052]

Resin powder constituent [of working example 1-3] for slush molding (S1) - (S3) and resin powder constituent (S4') - for slush molding of the comparative examples 1-3 (S6') were used, mold release resistance, an epidermis gross, metallic mold dirt nature, and melting nature were measured by the method shown below, and the result was shown in Table 1.

[0053]

[Table 1]

	実施例			比較例		
	1	2	3	1	2	3
離型抵抗(20ショット目) (kg/2.5cm)	0.3	0.3	0.3	0.3	0.3	0.3
離型抵抗(100ショット目) (kg/2.5cm)	0.5	0.5	0.4	2.7	3.0	3.3
表皮グロス(20ショット目)	1.8	1.7	1.8	1.8	1.8	1.7
表皮グロス(100ショット目)	2.1	2	2	1	0.9	0.9
金型汚れ性(100ショット目)	○	○	○	×	×	×
溶融性(20ショット目)	○	○	○	○	×	○

[0054]

<Valuation method>

- Mold release resistance

nickel electroforming pattern containing the crimp pattern beforehand heated by 270 °C was filled up with the resin powder constituent for slush molding, and the excessive resin powder constituent was discharged 10 seconds afterward. It was 270 °C, and also it heated and water-cooled for 90 seconds, and the skin (1 mm) was created. Where the obtained skin is stuck to a metallic mold, it cut to 2.5-cm width, and one end was removed, and it set to the autograph, it released from mold at the rate of 200 mm/min in the 90-degree direction to the mold face, and mold release resistance was measured.

Shaping was measured to the repetition deed 100 times, and mold release resistance was measured to the 20th shaping and the 100th time.

- Epidermis gross (gloss)

The 60-degree reflective gross (gloss) was measured about the outside skin after mold-release-resistance measurement.

- Metallic mold dirt nature

Visual observation of the change state on the surface of a metallic mold after mold-release-resistance measurement was carried out.

(Valuation basis)

O : with no discoloration

** : Those with discoloration

x : Discolor remarkably.

- Melting nature

The skin reverse side after mold-release-resistance measurement was observed visually, and melting nature was judged.

(Valuation basis)

O : it fuses uniformly and has gloss.

** : Although there is powder of non-melting in part, it has gloss.

x : It is lusterless at the rear face.

[Translation done.]